

Unraveling the Mystery

Livermore scientists are using the state-of-the-art computational power supplied by DOE's Accelerated Strategic Computing Initiative to increase understanding of high-explosive detonations.

In the study of weapons, a low explosive burns, but a high explosive detonates—a very different phenomenon. An initial shock compresses a high-explosive material, heating it and causing chemical decomposition. The formation of chemical products releases enormous amounts of energy in just billionths of a second. This process sustains the shock wave, which travels at supersonic velocity. All of this happens almost instantaneously to produce a blast of rapidly expanding hot gases.

In the brief instant of a high-explosive detonation, some remarkable events take place: the shock wave produces pressure up to 500,000 times that of Earth's atmosphere, the detonation wave travels as fast as 10 kilometers per second, temperatures can soar to 5,500 kelvins, and power approaches 20 billion watts per square centimeter.

Scientists at Livermore have been studying high explosives and modeling their behavior since the Laboratory was established because high explosives are an essential ingredient in every nuclear weapon. The first high

explosives used in nuclear weapons were relatively easy to model because their detonation occurred virtually instantaneously. For purposes of modeling, detonation was considered instantaneous, and experimental results matched the models very closely. But while these high explosives made the modeler's life easier, they were less safe to work with in the field because of their sensitivity to heat, impact, and other conditions.

About 20 years ago, less sensitive high explosives were developed that have significantly improved the safety and survivability of munitions, weapons, and personnel. TATB (1,3,5-triamino-2,4,6-trinitrobenzene), for instance, is virtually invulnerable to significant energy release in plane crashes, fires, and explosions or to deliberate attack with small arms fire. But this extreme insensitivity has its drawbacks. Initiating a TATB detonation is not easy. Detonation is still fast but by no means instantaneous. The resulting shock wave propagates

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differently from that of sensitive explosives, and the molecules that detonation produces are different. Using TATB and other insensitive high explosives effectively in weapon systems has required a more sophisticated understanding of the physics and chemistry of initiation and detonation.

Randy Simpson, explosives leader of the Stockpile Stewardship Program at Livermore, is coordinating efforts by several Livermore scientists to learn more about the detonation of these slower, insensitive high explosives. Their collective goal is to be able to model the detonation process as accurately as possible.

Getting Down to Fundamentals

For the Department of Energy's Stockpile Stewardship Program, Livermore is working to vastly improve the modeling of nuclear weapon performance. Without empirical results from nuclear testing, the models must

be based on first principles—the fundamental laws of physics—and data that can be gathered from nonnuclear tests. This reliance on developing much more accurate modeling capabilities extends to the high-explosive detonation phase.

The challenge for scientists who study explosive detonation is knowing—for an event that lasts less than a millionth of a second—the physics of each component over a wide range of pressures, densities, and temperatures and the way the components interact. This thermodynamic relationship of pressure, density, and internal energy for a given material is called its equation of state (EOS). Each of the components of a high-explosive detonation—hydrogen, nitrogen, oxygen, carbon, etc.—has its own EOS, as do the molecules that are various combinations of these elements. Behind the detonation front, the EOS of the

system is constantly evolving and changing, because the chemical composition is changing.

First-principles research is impossible without high-speed computers to perform the necessary number crunching. The calculations for even the simplest molecules are hugely time consuming. And the number of possible combinations rises rapidly as the number of atoms in the molecules grows or when the molecular changes are looked at over time. It is only with the massively parallel computers of the DOE's Accelerated Strategic Computing Initiative (ASCI) that this first-principles numerical work on high-explosives detonation is possible.

Simpson notes, "We now have the fastest computers anywhere in the world. The detonation properties of high explosives are a mystery, and it is only with the computational power of ASCI that we can hope to unravel the mystery."

Adding Kinetics to the Equation

ASCI is putting a new twist on research that has been under way for years by physicists and chemists at Livermore. Francis Ree, for instance, has been studying the products of high-explosive detonations for over 20 years and has, in the process, helped to develop CHEQ, a thermochemical code used to study the effects of fluid-phase separation on detonation. Larry Fried has been developing another thermochemical code, CHEETAH, which predicts the performance of explosives. CHEETAH specializes in multispecies chemical kinetics. Similarly, Jack Reaugh has been working with hydrodynamic codes for years. (Thermochemical codes use statistical mechanics and intermolecular

potentials to provide equations of state of reactive mixtures. Hydrodynamic codes describe material flow by solving the conservation laws of mass, momentum, and energy.)

Experimentalists, the “people who blow things up,” look at detonation at the macroscopic level. Ree’s and Fried’s teams work at the other end of the spectrum where individual molecules and atoms and their interactions are what matter. With his current research, Reaugh is in the middle, doing mesoscale simulations of the initiation process and exploring the effects of changes in the size of voids and grains of high explosives.

With ASCI and other high-powered computational capabilities, all three

teams can better understand their data and actually produce better data. In particular, they can address kinetics, including chemical kinetics (chemical changes over time) and mass transport kinetics, which are determined by material flow.

Traditional Chapman–Jouguet thermodynamic theory does not do a good job of modeling slow, or non-ideal, detonation processes. Chapman–Jouguet theory is essentially one-dimensional, which is fine for sensitive high-explosive detonations. It assumes that thermodynamic equilibrium of the detonation products is reached instantaneously and that all products are consumed completely. In fact, detonation of insensitive explosives is much more complicated. For one thing, it is three dimensional. For another, some chemical reactions occur more slowly than others. At the same time, a range of chemical reactions takes place during the decomposition of large high-explosive molecules into simple product molecules. The evolving equation of state for this collection of changing materials must somehow be represented. Adding kinetics to the equation is the key (Figure 1).

With the addition of kinetic information, Livermore’s hydrodynamic codes can be tied to its thermochemical codes to fully model the underlying physics and chemistry of a high-explosive detonation. Until recently, computer capabilities were such that three-dimensional hydrodynamic modeling had to be stripped of all chemistry. Now, with ASCI, the evolving chemistry can finally be addressed.

Complex Products

Francis Ree and his team are examining the molecules that are produced during detonation. An

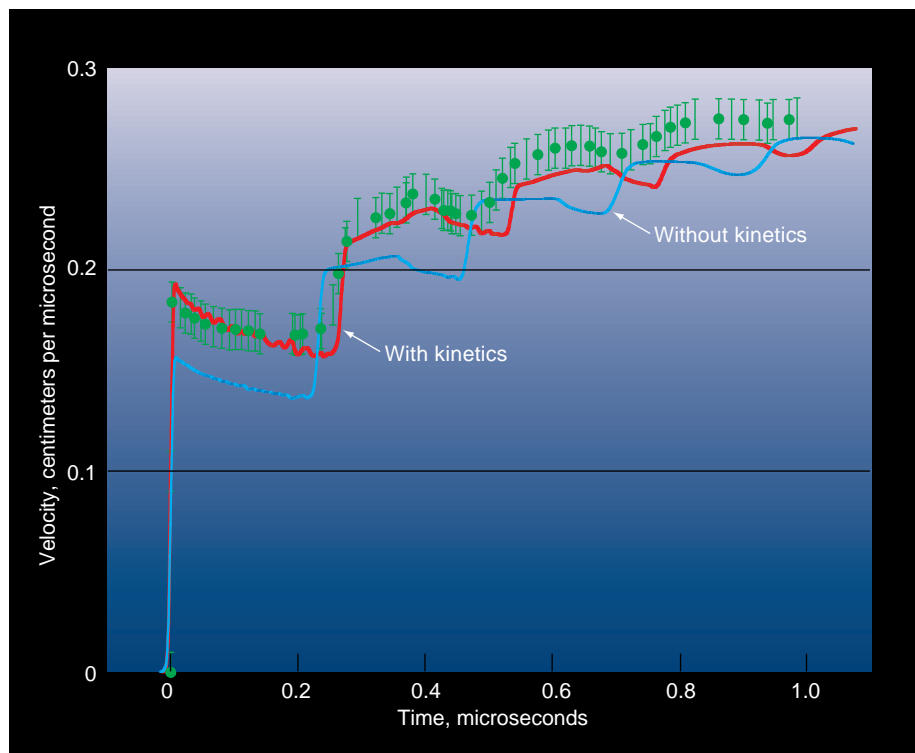


Figure 1. Adding kinetics to the CHEQ thermochemical code improves correlation with experimental results. Results from experiments run at Livermore’s Site 300 are shown with error bars, which much more closely match the code when kinetics of carbon coagulation has been incorporated. The velocity is that at the surface of a metal shocked by an explosive.

interesting aspect of this work is the phase changes that these products undergo as detonation proceeds. Last year, the team worked with scientists at the California Institute of Technology in Pasadena in an ASCI alliance. This year, they are collaborating with researchers at the University of North Carolina.

Ree says, "With conventional high explosives such as LX-14, which Livermore developed, the most important products behind the reaction zone are carbon dioxide, water, nitrogen, and carbon residues. But with insensitive high explosives, the product mix is more varied and involves more complex physics and chemistry."

Livermore's insensitive high explosives use fluorine in their binder. During detonation, the fluorine combines with hydrogen to make

gaseous hydrogen fluoride (HF), a highly corrosive compound and the strongest hydrogen bonding system occurring in nature. Moreover, insensitive high explosives produce large amounts of condensed carbon, which changes from graphite to diamond and then back to graphite. These explosives ultimately produce gases such as carbon dioxide when temperatures, pressures, and densities fall behind the detonation front. Accurate modeling of insensitive high explosives must consider both the thermodynamics of chemically reactive mixtures and the kinetics of carbon coagulation.

Predicting the performance of a high explosive requires information on all intermolecular potentials, which determine the forces of attraction and

repulsion acting between molecules, the dynamics of many possible chemical reactions, and such unusual phenomena as fluid–fluid phase separation (Figure 2). Calculating intermolecular potential is relatively simple in a pure stable gas such as nitrogen or carbon dioxide. In a gaseous mixture, the problem becomes more complex.

To handle the products of detonation, whose composition changes over time, the team developed CHEQ (chemical equilibrium) in 1984 to continually check the composition of a detonating mixture, pick the most stable mixture, and adjust the effective intermolecular potential accordingly.

No experimental data on HF exist at the conditions occurring during detonation because it is such a difficult

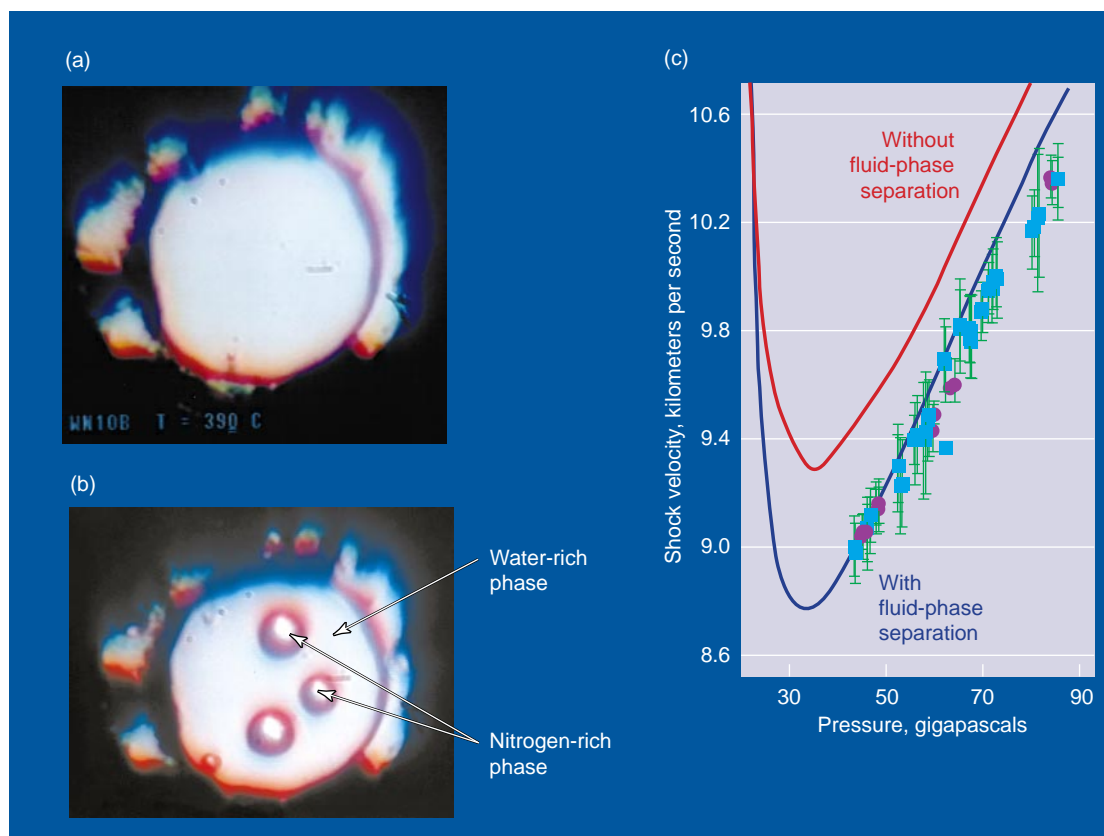


Figure 2. Using Livermore's diamond anvil cell, Marc Costantino has demonstrated fluid–fluid phase separation of water and nitrogen at high pressures and temperatures. (a) At 663 kelvins, a bubble of water and nitrogen may be seen. (b) When the temperature is lowered just slightly to 641 kelvins, the nitrogen and water separate. (c) When this fluid-phase separation is included in the CHEQ code, experimental results (error bars) closely match code predictions.

material to work with. There are, therefore, no data on intermolecular potentials between HF and other detonation products. In addition, there is no experimental information on potentials between nitrogen and carbon dioxide, carbon dioxide and water, and nitrogen and water at the pressures and temperatures relevant to explosive detonation. So, to establish intermolecular potentials between these detonation product species, Ree called in Livermore experts in quantum molecular dynamics Giulia Galli and Francois Gygi, who are using ASCI to perform simulations at high pressures and temperatures (Figure 3). By incorporating these potentials generated by computer into CHEQ, Ree's team will be able to produce reliable EOSs for several insensitive high explosives.

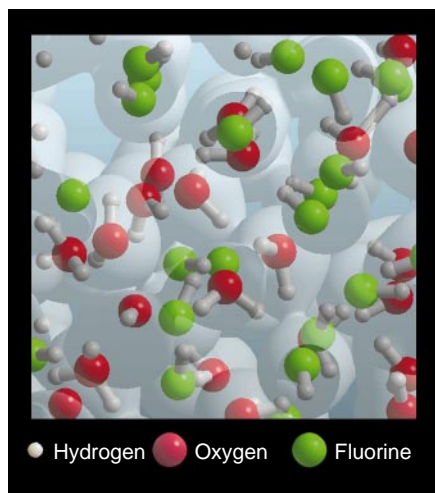


Figure 3. Quantum mechanical molecular dynamics results using Livermore's Accelerated Strategic Computing Initiative computer for hydrogen fluoride and water mixtures at 10 gigapascals and 600 kelvins. Computing 1 picosecond of real-time molecular activity took 372 hours of computing time, even with the most powerful computer in the world.

The relative leisureliness with which insensitive high explosives detonate is apparently caused in part by the slow release of energy from the carbon in them. During detonation, the free carbon coagulates into small clusters, which grow larger by diffusion. Because small carbon clusters have a larger surface area than larger clusters, a greater proportion of their energy is tied up in surface atom bonds. As the clusters agglomerate into larger and larger clusters, the fraction of energy in surface bonds decreases. Studies of carbon kinetics by Ree's team are directed at the slow diffusion kinetics of carbon clusters and the structural changes in the clusters (graphite to diamond and back to graphite).

To date, using molecular dynamics and Monte Carlo simulations, the team has computed the melting line of diamond and the line at which diamond liquefies. They are also studying the stability of diamond and graphite clusters, energy barriers between the two cluster types versus size, and kinetics of the graphite–diamond phase change. One result of this work is a better predictive model of high-explosive performance during detonation.

Multispecies Chemical Kinetics

Larry Fried and the CHEETAH team first incorporated a flexible kinetics capability into their thermochemical code in 1997. The code is particularly useful for dealing with complicated problems in which more than one chemical species is out of equilibrium. (See *S&TR*, November 1997, pp. 21–23.) Kinetic-rate laws were derived by matching dozens of measured curved detonation fronts. The result was the first general-purpose kinetics capability applicable to a broad range of slowly reacting explosives.

Currently, the team is combining kinetics with sophisticated molecular equations of state. The EOSs are based on massive statistical mechanics calculations performed on the ASCI supercomputer and validated with EOS experimental data, including information on static compression and shock. Says Fried, "Our goal is to produce molecular equations of state that are accurate over the broadest range of thermodynamic conditions possible, including relatively cold states of only a few hundred kelvins. Such states have not been well modeled by traditional thermochemical codes." Fried and his coworkers have also developed a way to infer the equation of state of hydrogen fluoride and other difficult molecules from high-pressure shock experiments performed on plastics. Only recently did researchers realize that these experiments contained "keys" to the EOS of hydrogen fluoride and hydrogen chloride, materials that are difficult to study in isolation.

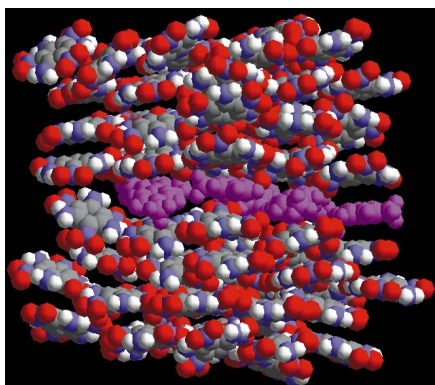
CHEETAH's kinetics calculations offer the most detailed picture possible of chemical compositions through the high-explosive reaction zone. Because this level of detail is difficult to include in large-scale hydrodynamic simulations, the team is producing simplified reactive flow models that incorporate reaction rates calculated with the more detailed CHEETAH. The simplified models will be used in three-dimensional hydrodynamic calculations with billions of zones.

ASCI's computers are being used to produce basic science data for CHEETAH where massive statistical calculations are required. And they will continue to become more powerful. Fried noted that in its current configuration, ASCI computers can handle much more difficult calculations than it could a year ago. This improved capability will allow the team to

develop accurate models for highly charged molecules such as water and hydrogen fluoride.

The team is also interested in understanding how chemical impurities in high explosives affect their detonation, safety, and aging properties. In the past, the effects of impurities on high explosives were not carefully studied.

(a)



(b)

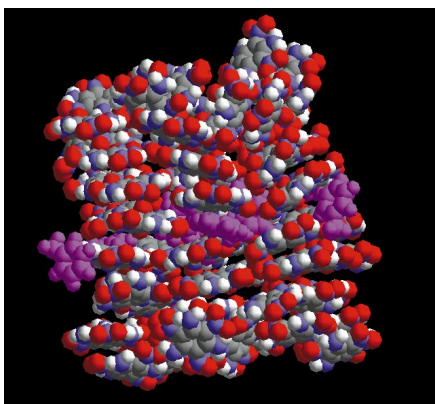


Figure 4. Studies of toluene impurities and the insensitive high explosive TATB are important because toluene is the major volatile chemical released from industrial TATB. (a) At room temperature, the toluene impurities are locked into the TATB. (b) At 500 kelvins, they are released from the TATB lattice. These impurities are especially important in the aging of TATB.

ASCI resources make it possible to study these problems in detail.

Figure 4 shows a simulation of a toluene release from TATB. At room temperature, the simulation indicates that toluene is “locked” in TATB. When heated to 500 kelvins, however, the toluene is released from the TATB lattice. These calculations help explain experiments where large quantities of toluene are released when TATB is exposed to strong sound waves.

In the future, Fried expects to link CHEETAH directly to ASCI’s hydrodynamic codes. CHEETAH has been linked to smaller hydro codes, but not to massively parallel codes such as ARES and ALE3D. Fried is also considering developing a version of CHEETAH that would run exclusively on ASCI. For CHEETAH to perform Monte Carlo statistical calculations, ASCI’s computing power is essential.

A Look at Initiation

We usually think that perfect things work better. But in high explosives,

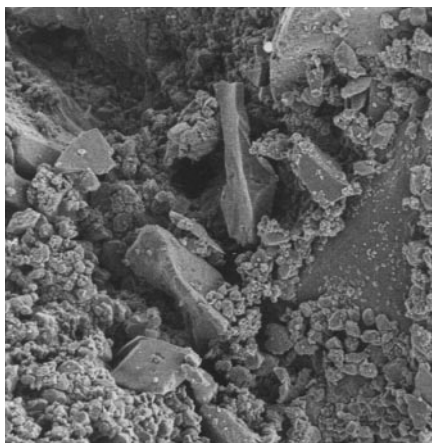


Figure 5. High-explosive materials contain crystalline explosives, binders, plasticizers, and porosity. The voids and other irregularities are necessary for explosives to perform properly.

defects are important to their performance. In some cases, pure, homogenized high explosives do not get sufficiently hot at the shock front to react rapidly enough for detonation. Instead, porosity, impedance mismatches between explosive components, and intracrystalline defects in the high explosive, binder, and other materials are essential. They cause localized hot spots that drive the decomposition reactions (**Figure 5**).

According to Jack Reaugh, “These temperature spikes are visible in liquid high explosives as bubbles where ignition takes place. With solid high explosives, we know the hot spots are there, but they are not visible. So simulations are necessary to ‘see’ the phenomenon.”

If the voids are too small, heat diffuses too quickly, and the mixture will not ignite. Reaugh’s challenge is to quantify what size is best, both for voids and for the particles around them, to maximize the accuracy of reactive flow models.

His work started in early 1999, and his focus initially is on modeling small parts of a detonation’s initiation at the grain scale. Some of his first results are illustrated in **Figure 6**, which shows a block of high-explosive particles and the binder between them at three points just after initiation. As the shock front moves through the block, it compresses the mixture.

For these pictures to be meaningful, Reaugh must first develop models of all materials involved prior to ignition, that is, the EOS of the unreacted high explosive, binder, and air that fills the voids. Then he must incorporate such information as temperatures, the thermal conductivity of the unreacted materials, heat transfer, and chemical reactions that take place as initiation is occurring. Each of these processes has a model associated with it, and at the moment, not all the

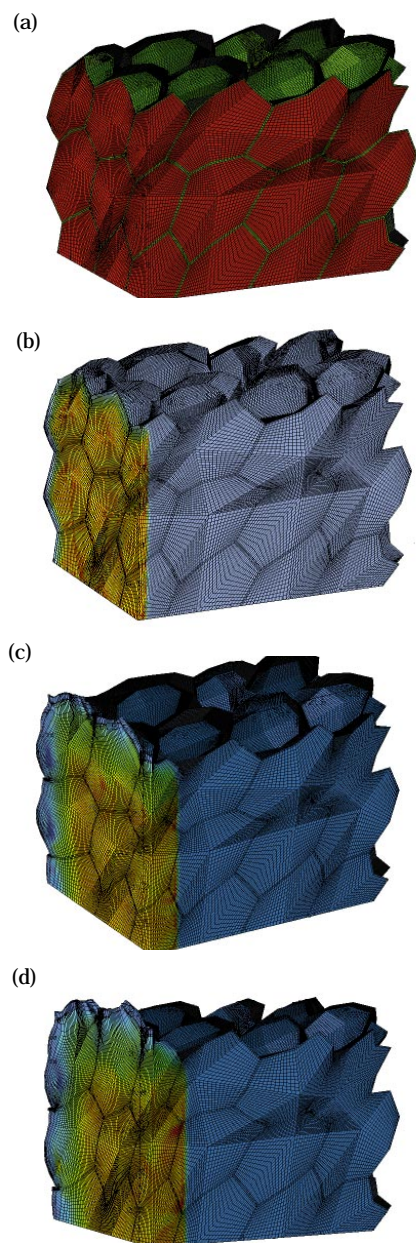


Figure 6. (a) A tiny block of high explosives, just four by three by three particles, with binder locking the particles together, prior to detonation. (b), (c), and (d) The block of high explosive shown at three moments immediately following initiation. The shock wave compresses the particles as it moves through the material.

information needed is available. For the time being, he is making do with bare-bones models that use available data and is running his simulations on Livermore's three-dimensional hydrodynamic code ALE3D.

Unlike Ree, who is looking at the products of detonation, Reaugh is studying the front end. According to Reaugh, "The really interesting stuff goes on in the first moments after detonation." His work will give the closest look yet at how initiation occurs, how long it takes, how reactions occur, whether full reaction occurs, and so on.

His simulations are just now getting big enough that he needs to use ASCI. When they include just a few particles, a smaller computer is adequate. ASCI makes possible larger, more complex simulations that show "the really interesting stuff."

With Even Faster Computing

Says Simpson, "ASCI's computational power is enormous. It

allows us to simulate high-explosive detonation to a level of detail unimaginable even a few years ago. By effectively incorporating kinetics into our models, we will not only be able to describe what is occurring in a high-explosive detonation, but will also be able to predict what will happen over time. That is a huge improvement over current modeling capabilities." With better models will come increased performance, safety, and reliability of the high explosives on which stockpiled weapons rely.

—Katie Walter

Key Words: Accelerated Strategic Computing Initiative (ASCI), CHEETAH, CHEQ, detonation, equation of state (EOS), high explosives, hydrodynamic codes, initiation, insensitive high explosives, multispecies chemical kinetics, thermochemical codes.

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About the Scientists



Like all science done at Lawrence Livermore, modeling the details of slower, insensitive high explosive detonations requires a multidisciplinary team. Leading this work is **RANDY SIMPSON** (left), explosives leader of the Stockpile Stewardship Program at Livermore. Other principals include chemist **LARRY FRIED** (second from right), one of the primary developers of the CHEETAH code, which Fried and his colleagues are developing to accurately model the molecular equations of state of explosive materials over a broad range of thermodynamic conditions.

Physicist **FRANCIS REE** (right) and his team are refining the physics models in the CHEQ code to study the products of insensitive explosives as they are generated and change during detonation. Physicist **JACK REAUGH** (second from left) and his associates are concentrating not on the products of detonation but on the process of initiation. They are simulating the imperfections of an explosive's components during the first moments of detonation to determine how the interactions of these imperfections drive the detonation.